The Structure of Tungsten Oxide Tetrafluoride

By I. R. Beattie* and D. J. Reynolds
(Department of Chemistry, The University, Southampton, SO9 5NH)

From single crystal *X*-ray studies it has recently been suggested[1] that WOF_4 is an oxygen-bridged tetramer (in contrast to $MoOF_4$ which is apparently fluorine bridged).[2] The systematic absences were found to be characteristic of the space groups *C*2, *Cm*, or *C*2/*m*. Assignment of atomic positions in cases where there is one very heavy atom (W) and two closely similar light atoms (O and F) is difficult without accurate intensity data. Even with accurate data if some disordering of the light atoms occurs it is possible to make erroneous deductions. The final *R* value for WOF_4 was 0·128. It is clear that correct placing of the tungsten atoms, together with oxygen or fluorine in any of the "correct" light atom positions, could easily lead to an *R* value of this order.

In this report of the *X*-ray analysis,[1] some infrared data are also given. In particular, a band at 1050 cm.$^{-1}$ is assigned to a W–F stretching frequency, with a force constant of about 10 mdyne Å^{-1} for a bond distance of 1·65 Å. This suggestion is untenable. In NbF_5 and TaF_5 (which are structurally similar[3] to WOF_4) no fundamental higher than 766 cm.$^{-1}$ is observed.[4] In MoF_6 and WF_6 no band higher than 769 cm.$^{-1}$ is observed.[5] The band at 1050 cm.^{1} is thus either a terminal or a bridging oxygen mode. Although the distinction between terminal and bridge oxygens by infrared spectroscopy is not clear cut, nonetheless, a value of 1050 cm.$^{-1}$ for a bridging oxygen mode would be uniquely high.

The solid-state Raman spectrum of WOF_4 shows the following bands: *1058*vs, 744w, *728*m, 705vvw, 663vw, 563vvw, 523vvw, 330sh, 318sh, *314*m, 265vw,) 242vw, and 215vw (principal bands being italicised). The band at 1058 cm.$^{-1}$ is strongly indicative of a terminal oxygen from its position, half-width (about 7 cm.$^{-1}$) and intensity.

The melt Raman spectrum shows striking similarities to the solid-state spectra: 1058vspol, 730spol, 680wpol, and 312m. The bands in the region of 700 cm.$^{-1}$ are clearly terminal fluorine stretching modes. The similarity between solid state and melt spectra strongly suggests a similar structure in the two states. It is thus necessary to explain the presence of an intense, strongly polarised ($\rho_{\text{n}} \approx$ O) band at 1056 cm.$^{-1}$.

In view of the position of this band, if it is a fundamental, it can arise only from a M=O or an (approximately) linear M–O–M vibration (regarding M here as an infinite mass and neglecting F-matrix coupling). The ρ_n value for a terminal oxygen stretching mode would be expected to be low and the Raman intensity would be expected to be high. On the other hand for the "free" linear species M–O–M the antisymmetric stretching mode is formally Raman inactive. Slight distortion may render this band weakly Raman active normally with a ρ_n value of $\frac{6}{7}$. In a tetrameric species, such as that under discussion, this band would be weak and depolarised. It is thus probable that the appearance of an intense, narrow, strongly polarised line in the 1000 cm.$^{-1}$ region in Raman spectra of melts of oxides or oxide halides will be found to be characteristic of terminal oxygens—providing that the metal concerned is heavy relative to oxygen. Our conclusion is that WOF_4 is a fluorine-bridged polymer in the solid state and in the melt (although we cannot exclude the possibility of *some* oxygen bridging). Confirmation of this supposition is supplied by the fact that $MoOF_4$ (which is reported to be fluorine bridged by *X*-ray) shows an intense narrow band at 1042 cm.$^{-1}$ in the solid state, shifting to 1039 cm.$^{-1}$ in the melt (where it is strongly polarised). The relevant melt spectrum for $MoOF_4$ (compare WOF_4) is: 1038 vspol, 712 vspol, 665 mpol, 314, 308 s, and 244 broad.

(*Received, October 14th,* 1968; *Com.* 1395.)

---

[1] A. J. Edwards and G. R. Jones, *J. Chem. Soc.*, 1968, 2075.

[2] A. J. Edwards, G. R. Jones, and B. R. Steventon, *Chem. Comm.*, 1967, 462.

[3] A. J. Edwards, *J. Chem. Soc.*, 1964, 3714.

[4] I. R. Beattie, K. Livingstone, G. A. Ozin, and D. J. Reynolds, *J. Chem. Soc.* (*A*), to be published.

[5] D. Adams, "Metal Ligand and Related Vibrations", Edward Arnold, London, 1967.